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M. Mogren Al-Mogren, M. L. Senent, and M. Hochlaf

Theoretical characterization of C_7, C_7^-, and C_7^+

M. Mogren Al-Mogren,[1,a)] M. L. Senent,[2,b)] and M. Hochlaf[3,c)]
[1]*Chemistry Department, Faculty of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Kingdom of Saudi Arabia*
[2]*Departamento de Química y Física Teóricas, Instituto de Estructura de la Materia, IEM-C.S.I.C., Serrano 121, Madrid 28006, Spain*
[3]*Laboratoire de Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, Université Paris-Est, 5 boulevard Descartes, 77454 Marne-la-Vallée, France*

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We present a theoretical investigation of neutral and ionic C_7 molecules. Since carbon chains present isomerism and the number of possible structures increases fast with the number of carbon atoms, a B3LYP/aug-cc-pVTZ search of stationary points has been achieved. For C_7, we found twelve minimal structures. Among these forms, eleven C_7 isomers are located into the lowest singlet hyper potential energy surface. The most stable form of C_7 is linear and possesses a $^1\Sigma_g^+$ symmetry species. For C_7^-, we characterized fifteen stable forms, where twelve are of doublet spin-multiplicity. The global minimum of C_7^- is a $^2\Pi_g$ doubly degenerate Renner-Teller structure. For C_7^+ cation, we found eleven doublet and three quartet isomers with a 7-atom cycle, C_7^+ (X^2A_1) ground state. For the most stable forms, explicitly correlated (R)CCSD(T)-F12 calculations have been performed for the determination of equilibrium geometries and for the spectroscopic characterization of C_7, C_7^-, and C_7^+, providing accurate rotational constants and harmonic frequencies. Vertical excitation energies to the lowest electronic states have been computed at the CASSCF/MRCI/aug-cc-pVTZ level. Thirty five electronic states of C_7, suitable of being involved in reactive processes, lie below 7 eV. Fourteen metastable electronic states of C_7^- have been found below 3.5 eV. For *linear*-C_7, we compute the electron affinity and the ionization energy to be 3.38 eV and 10.42 eV, respectively. [http://dx.doi.org/10.1063/1.4817199]

INTRODUCTION

During the 1980s decade, C_n carbon chains were proposed as responsible for the Diffuse Interstellar Bands (DIBs),[1] and started to be considered as relevant species for astrophysics. Commonly, they appear in astrochemical models as important intermediates of reactions involving carbon compounds such as polycyclic aromatic hydrocarbons (PAHs). Small chains are considered as building blocks of larger species such as the fullerenes. Pure carbon chains are abundant species in carbon rich circumstellar envelopes.[2]

In spite of their astrophysical relevance, few bare chains have been observed in gas phase extraterrestrial sources. The reasons of that can be the absence of permanent dipole moments indispensable for radioastronomical observations and the lack of well characterized molecular properties. The shortest chain C_2, discovered in Cygnus OB2,[3] was the first one detected, followed by C_3 and *linear*-C_5 found in IRC+10216[4–6] and Sagittarius B2.[5] Detections were performed through the analysis of infrared active vibrational excitations or through their electronic transitions.

Neutral and charged pure carbon chains are known to exist in a rich variety of structures, including chains and monocyclic and polycyclic rings.[7] Many of them are highly reactive and extremely difficult to treat at the laboratory level. Smaller species have been studied using different theoretical and experimental techniques such as *ab initio* calculations,[8–13] high resolution infrared spectroscopy in gas phase or solid matrices,[14–23] vibrationally resolved photoelectron spectroscopy,[24] optical emission and absorption spectroscopy in solid matrices and gas phase,[25–29] and multiphoton electron detachment techniques.[7] Gas phase electronic spectral data can be compared directly with astrophysical observations.[25,30]

Detailed presentation of previous studies treating neutral, cationic, and anionic C_7 can be found in van Orden and Saykally[7] and Jochnowitz and Maier[25] reviews, and in Refs. 8–24 and 26–29. Briefly, the structure of neutral *linear*-C_7 and various monosubstituted ^{13}C-isotopologues has been investigated using coupled-cluster with single, double, and triple substitutions (CCSD(T)) theory concluding that no evidence of floppiness appears.[13] Rotational constants (B_e = 916.8 MHz and B_0 = 919.0 MHz), as well as some anharmonic spectroscopic parameters are provided.[13] Vertical excitations to the lowest electronic states of the neutral form have been computed by Kolbuszewski[8] and Giuffreda *et al.*,[12] whereas electronic states of *linear*-C_7^- were determined by Lakin *et al.*[10] and Cao *et al.*[11] The spin-orbit constant of C_7^- ($X^2\Pi_g$) was estimated to be $A_{so} = 26.8\ cm^{-1}$ by Lakin *et al.*[10] Large scale coupled cluster calculations have been used to find the equilibrium structure of *linear*-C_7^-.

The infrared spectrum of neutral C_7 was studied first in neon and argon matrices and, more recently, in gas phase.[14–23] C_7 presents eleven vibrational modes, five of them lying below 500 cm^{-1}. Very recently, the infrared active modes $\nu_4(\sigma_u)$

a)E-mail: mmogren@ksu.edu.sa
b)E-mail: senent@iem.cfmac.csic.es
c)E-mail: hochlaf@univ-mlv.fr

and $\nu_5(\sigma_u)$ were precisely measured using high resolution spectroscopy.[21–23] The two band centers were localized at 2138.38 cm^{-1} and 1898.44 cm^{-1}, respectively.

The interpretation of DIBs nature has generated electronic spectra studies of C_7 and C_7^-,[25,29] although astrophysical observations rejected the C_7^- diffuse interstellar band hypothesis on the basis of laboratory measurements.[30] The $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and $^1\Pi_g \leftarrow X^1\Sigma_g^+$ electronic absorption transitions corresponding to the neutral form trapped in Ne matrices were analyzed by Maier and co-workers.[26] The band centers are localized at 39 556 cm^{-1} and 18 440 cm^{-1}.[26] Using anion photoelectron spectroscopy, Kohno *et al.*[28] observed a band at 1.71 eV, which they tentatively assigned to a triplet state of $^3\Sigma_u^+$, $^3\Sigma_u^-$, or $^3\Delta_u$ symmetry. For C_7^- anion, electronic transitions from $X^2\Pi_g$ to three doublet electronic states of $^2\Pi_u$ symmetry were measured by Tulej *et al.*[25,29]

The present paper tries to give a complete characterization of the molecule covering different aspects for which there is lack of available information. Therefore, we describe a rigorous and systematic theoretical study of the seven atom carbon chain C_7, as well as its corresponding charged species C_7^- and C_7^+. This work and its methodology follow previous studies on other carbon chains performed using highly correlated *ab initio* methods.[31–38] As bare carbon chains present isomerism, we started our investigations by a detailed search of equilibrium structures. Some of them are undetectable forms given their low stability, but they can be important intermediates during reactive processes in combustion and in astrophysical media. For the most stable forms, we used explicitly correlated methods to compute structural parameters and rotational constants. Since carbon chains present a large density of electronic states close to the ground state, we have determined, using multi reference configuration interaction theory, vertical excitation energies to the lowest states, which can be involved in the reactivity.[38]

This paper is organized as follows: First, we detail the computational methods used. Then, we present our results ((R)CCSD(T) calculations of the isomers, structure, and (R)CCSD(T)-F12 equilibrium spectroscopic parameters of the most stable forms and multi reference configuration interaction approach (MRCI) electronic vertical excitations) and their comparison to previous experimental and theoretical[8–13] works. As the number of isomers is too large, B3LYP results of the preliminary search of stationary points are provided in the supplementary material.[58]

COMPUTATIONAL DETAILS

The preliminary search of C_7, C_7^-, and C_7^+ minimum energy structures and transitions states was carried out with the code GAUSSIAN 09,[39] density functional theory with the B3LYP functional,[40,41] and the aug-cc-pVTZ basis set.[42] For the equilibrium molecular structure optimizations, we used the standard options as implemented in the GAUSSIAN code. Later on, the energies of all structures were refined by performing single point calculations on the B3LYP geometries using restricted coupled cluster theory with a perturbative treatment of triple excitations (RCCSD(T)).[43] Afterwards, the most relevant structures and their spectroscopy parameters were computed using explicitly correlated coupled cluster theory RCCSD(T)-F12.[44] For these last calculations, three basis sets were employed: the orbital aug-cc-pVTZ, an aVTZ-MP2FIT basis set for the density fitting integral evaluation of the F12 integrals, and the VTZ/JKFIT basis set because the many electron integrals are approximated by resolutions of the identity expansions.[45] As previously established (Refs. 51–57, and references therein), the (R)CCSD(T)-F12/aug-cc-pVTZ accuracy reaches the RCCSD(T)/aug-cc-pV5Z precision, but by means of a relatively low computational effort. Therefore, it represents a very efficient level of theory for accurate characterizations of detectable molecular species.

For the (R)CCSD(T) and (R)CCSD(T)-F12 calculations and for the determination of vertical electronic excitations, we used the MOLPRO program suite.[46] Electron affinities, vertical and adiabatic excitation energies to the excited electronic states were determined with the complete active space self-consistent field (CASSCF) method,[47,48] followed by the internally contracted MRCI.[49,50] For the linear forms, in the CASSCF calculations, the lowest seven σ_g, two π_u, and seven σ_u molecular orbitals (MOs) were kept doubly occupied, and we considered the upper three σ_g, four π_u, two σ_u, and four π_g MOs as active defining an active space of 13 active orbitals and 12 electrons for neutral C_7, 13 electrons for C_7^-, and 11 electrons for C_7^+. For *cyclic*-C_7^+ (XII-isomer, see below), the lowest eight a_1, one b_1, and six b_2 MOs were kept doubly occupied and we considered the upper five a_1, three b_1, three b_2, and two a_2 MOs as active.

RESULTS AND DISCUSSION

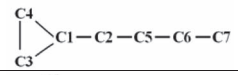
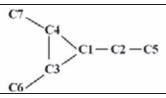
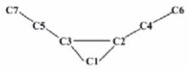
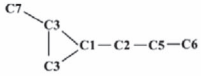
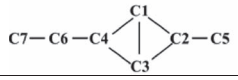
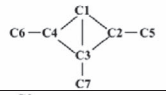
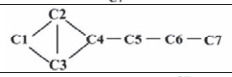
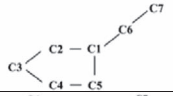
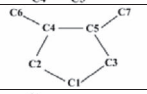
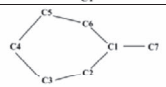
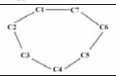
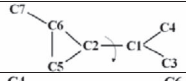
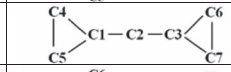
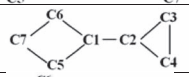
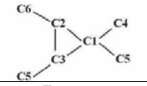
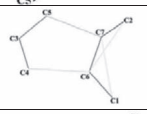
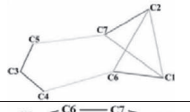
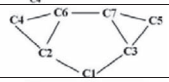
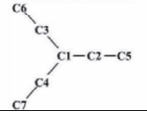
Stationary points, spectroscopic parameters, electron affinity, and ionization energy

Eighteen, nineteen, and twenty different stationary structures of C_7, C_7^-, and C_7^+ have been found after a systematic search performed with B3LYP/aug-cc-pVTZ. The corresponding energies, structural parameters, dipole moments, rotational constants, and harmonic frequencies are provided as the supplementary material.[58] At this level of theory, twelve C_7 structures correspond to minimum equilibrium geometries (M). The remaining ones are transition states (TS). The charged species, C_7^- and C_7^+, reveal fifteen and fourteen minima, respectively. The main set of C_7 isomers (a total of eleven structures) shows singlet ground electronic states, whereas C_7^- and C_7^+ display twelve and eleven isomers with ground states of doublet spin multiplicities.

To perform a systematic and complete search of isomers, we have designed all the possible structures that can be formed with seven identical carbon atoms, starting by the linear form followed by geometries containing cycles of three, four, five, six, and seven atoms. For each case, the geometry optimization has been performed using the largest symmetry group and all the sub-groups and different spin multiplicities.

To obtain more accurate relative stabilities, (R)CCSD(T)/aug-cc-pVTZ single point calculations were achieved on all density functional structures (DFT) structures. (R)CCSD(T) relative energies are shown in Table I. Lower energy isomers

TABLE I. C_7 isomers (M) and transition states (TS) calculated with (R)CCSD(T)/aug-cc-pVTZ. Relative energies (Er) are in eV.

Isomers and transitions states		C_7	C_7^-	C_7^+
I-C_7 ($D_{\infty h}$)		M - $X^1\Sigma_g^+$ E=-265.851777a.u. Er=0.0	M - $X^2\Pi_g$ E=-265.971996 a.u. Er=0.0	M - $X^2\Sigma_u^+$ E=-265.466543 a.u. Er=0.0
II-C_7 (C_{2v})		TS - X^1A_1 Er=1.25	M - X^2B_2 Er=0.72	M - X^4A_2 Er=1.85
III-C_7 (C_{2v})		M - X^1A_1 Er=3.77	M - X^4A_1 Er=4.94	M - X^2A_2 Er=4.03
IV-C_7 (C_{2v})			M - X^2A_1 Er=1.26	M-X^4B_2 Er=2.03
V-C_7 (C_s)		M - X^1A' Er=2.82	M-X^4A' Er=3.68	M - X^2A'' Er=2.19
VI-C_7 (C_{2v})		M - X^1A_1 Er=3.13	M - X^2B_2 Er=2.79	M - X^2B_1 Er=2.52
VII-C_7 (C_{2v})		TS - X^1A_1 Er=5.53	TS - X^2B_2 E=5.92	TS - X^2A_1 Er=4.78
VIII-C_7 (C_{2v})		M - X^1A_1 Er=1.79	M - X^2B_2 Er=1.90	M - X^2A_1 Er=1.26
IX-C_7 (C_s)		TS – X^3A'' Er=6.21	M - X^2A' Er=3.48	M - X^2A'' Er=2.72
X-C_7 (C_{2v})				M - X^2B_2 Er=3.56
XI-C_7 (C_{2v})		M - X^3B_2 Er=3.09	M - X^2B_2 Er=2.94	M - X^4B_2 Er=2.69
XII-C_7 (C_{2v})		M - X^1A_1 Er=0.52	TS - X^2B_1 Er=2.13	TS - X^2A_1 Er=-1.55
XIII-C_7 (C_s)		M - X^1A' Er=3.54	M - X^2A'' Er=3.22	M - X^4A'' (C_s) Er=3.71
XIV-C_7		TS - X^1A (D_2) Er=2.39	M -X^2B_{3g} (D_{2h}) Er=2.09	TS-X^4B_{1g} (D_{2h}) Er= 2.50
XV-C_7 (C_{2v})		M - X^1A_1 Er=2.45	M - X^2B_1 Er=3,43	TS - X^2A_1 Er=2.15
XVI-C_7 (C_{2v})		TS - X^1A_1 Er=5.20	M-X^4A_2 Er=5.55	TS - X^2B_2 Er=6.75
XVII-C_7 (C_{2v})		M - X^1A_1 Er=4.51	M - X^2A_1 Er=4.59	M - X^2B_2 Er=3.96
XVIII-C_7 (C_{2v})		TS - X^3B_1 Er=4.54	TS - X^2B_1 Er=4.51	TS - X^2B_1 Er=3.56
XIX-C_7 (C2v)		M - X^1A_1 Er=2.70	TS - X^2A_1 Er=3.37	M - X^4A_2 Er=2.21
XX-C_7 (D_{3h})		M - X^1A_1' Er=4.91	M - X^2A_2' Er=3.09	M - X^4A_2' Er=3.73

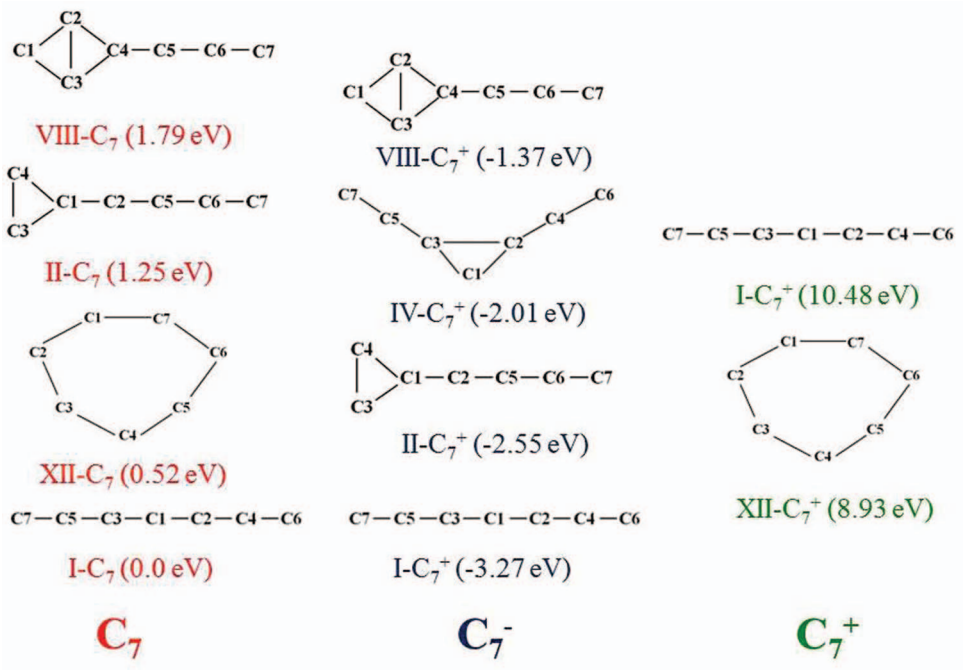


FIG. 1. The low energy structures of C_7, C_7^-, and C_7^+; RCCSD(T)/aug-cc-pVTZ relative energies are referred to *l*-C_7 (in eV).

are shown in Figure 1. The most stable geometries of the neutral and anion species are two linear forms, I-C_7 ($X^1\Sigma_g^+$) and I-C_7^-($X^2\Pi_g$) (or *l*-C_7 and *l*-C_7^-), and for the cation, the lowest energy corresponds to a 7-atom cyclic structure XII-C_7^+ (X^2A_1) (or c-C_7^+). This last one displays an imaginary frequency when it is calculated with B3LYP (see the supplementary material[58] where it is classified, such as TS). Since MP2 and highly correlated RCCSD(T) calculations lead to a minimum instead to a TS. The imaginary frequency at DFT level can be related to a lack of electronic correlation. The effect of dynamical correlation on carbon chain isomer relative energy was already evidenced for C_6.[35] In Table II, some RCCSD(T)-F12 structural and spectroscopic properties corresponding to the three linear forms, I-C_7, I-C_7^-, and I-C_7^+ and to the cyclic XII-C_7^+, are shown. Three of these structures, I-C_7, I-C_7^-, and XII-C_7^+, represent the minimum energy geometries. I-C_7^+ is an equilibrium geometry lying at 1.57 eV over XII-C_7^+.

For carbon chains, the number of stable geometries increases fast with the number of carbons. In our previous papers, we found a total of 2, 3, and 3 isomers for C_4, C_4^-, and C_4^+, respectively;[31,34,36] 4 for C_5;[33] and 9 and 7 for C_6 and C_6^-, respectively.[35,37] For short neutral C_n chains, it is generally accepted that those with even n show two isomers, one cyclic and one linear of similar stabilities but of different spin multiplicities. When n is odd,[7] a single prominent stable structure is found. Our previous calculations for $n < 7$ species[31,33–37] show that these species obey this rule. Indeed, the most stable forms of C_4 and C_6 are singlet cycles of four and six atoms followed by triplet linear ones showing relative energies of 0.07 eV and 0.5 eV, respectively. In the case of C_5, the prominence of the singlet linear form is evident, since the following isomer lies over 2.6 eV. Similar to C_5, the favorable lowest geometry of C_7 is linear (I-C_7 or *l*-C_7). However, the relative energy of the following cyclic isomer (XII-C_7 or c-C_7) is very low (0.5 eV) as for C_6. Both isomers I-C_7 and XII-C_7 show singlet ground electronic states. C_7 presents hence mixed isomeric properties of odd and even carbon chains.

Electron-affinities of *l*-C_4 and *l*-C_6 were calculated to be 3.82 eV and 4.16 eV[38] at the (R)CCSD(T)/aug-cc-pVTZ level of theory. These values are close to the experimental values of 3.882 eV and 4.185 eV.[24] At this level of calculation, *l*-C_7 electron affinity is computed to be 3.27 eV, which is off by ∼0.01 eV from the experimental value (3.358 eV[24]). The large electron affinity of C_7 is on line with the stabilization of linear carbon chains with electron attachment to form linear anions. The latter ones are highly more stable than the remaining negatively charged isomers.[34,37,38] *A priori*, this is one of the reasons for which negative carbon chains were the first detected in astrophysical media.[38] Therefore, C_7 and C_7^- are good candidates to be present there. At the (R)CCSD(T)-F12 level, the I-C_7 electron affinity (EA) has been determined to be 3.32 eV. This value switches to 3.38 eV when the zero point vibrational energy correction is considered and can be compared with the photoelectron spectroscopy value, EA = 3.358 eV.[24]

Anion C_7^- shows three isomers with relative energies with respect to the linear form lower than 2 eV (see Figure 1). They correspond to II-C_7^- (Er = 0.72 eV), IV-C_7^- (Er = 1.26 eV) and VIII-C_7^- (Er = 1.90 eV). The C_7 energy difference between the two first isomers, I-C_7^- and II-C_7^- (0.72 eV) is lower than for C_4 (1.34 eV) and C_6 (1.15 eV). We can conclude that, although *l*-C_7^- is really stable, it is less prominently stable than *l*-C_4^- and *l*-C_6^-.

Dynamical electron correlation included in our post Hartree-Fock computations plays a crucial role on the relative stabilities of the cation isomers. With density functional

TABLE II. Total electronic energies (E, in a.u.), relative energies (E_r, in eV), bond distances (in Å), equilibrium rotational constants (in MHz), harmonic fundamental frequencies (ω, in cm^{-1}), electron affinity (EA, in eV), and ionization energy (IE, in eV) of the linear *l*-C_7, *l*-C_7^-, and *l*-C_7^+ and of the c-C_7^+ isomer calculated with RCCSD(T)-F12/aug-ccpVTZ.

l-C_7 ($X^1\Sigma_g^+$) (I-C_7)					
	Calc.	Expt. [Ref. #, g, m][a]		Calc.	Expt. [Ref. #, g, m][a]
E	− 265.915226		$\omega_4(\sigma_u)$	2200.1	2138.315 [Refs. 14, 16, and 21, g]
E_r	0.0				2134.6 [Refs. 17, 22, and 26, m]; 2127.8 [Ref. 18, m]; 2120.4 [Ref. 19, m]
EA	3.38	3.358 [Ref. 24]			
IE ($l \rightarrow l^+$)	10.42		$\omega_5(\sigma_u)$	1931.6	1898.378 [Refs. 15 and 23, g]
IE ($l \rightarrow c^+$)	9.1				1897.5 [Refs. 17, 22, and 26, m]; 1894.2 [Ref. 18, m]; 1889.3 [Ref. 19, m]
B_e	911.792	917.755 [Ref. 16]	$\omega_6(\sigma_u)$	1088.1	
C1-C2	1.2756		$\omega_7(\pi_g)$	469.6	496 ± 110 [Ref. 24, g]
C2-C4	1.2900		$\omega_8(\pi_g)$	147.2	
C4-C6	1.2925		$\omega_9(\pi_u)$	460.5	
$\omega_1(\sigma_g)$	2166.5		$\omega_{10}(\pi_u)$	227.7	
$\omega_2(\sigma_g)$	1564.4		$\omega_{11}(\pi_u)$	63.9	
$\omega_3(\sigma_g)$	574.9	548 ± 90 [Ref. 24, g] 582 [Ref. 19, m]			

l-C_7^- ($X^2\Pi_g$) (I-C_7^-)			
	Calc.		Calc.
E	− 266.037098	$\omega(\sigma_g)$	3148.6; 2027.5; 840.8
E_r	0.0	$\omega(\sigma_u)$	4896.1; 2568.9; 647.9
B_e	901.579	$\omega(\pi_g)$	486.5; 488.9; 174.1; 180.5
C1-C2	1.2801	$\omega(\pi_u)$	345.3; 359.7; 260.9; 263.7; 76.8; 70
C2-C4	1.3111		
C4-C6	1.2823		

l-C_7^+ ($^2\Sigma_u^+$) (I-C_7^+)			
	Calc.		Calc.
E	− 265.532170	C1-C2	1.2754
E_r	1.57	C2-C4	1.2955
B_e	914.563	C4-C6	1.2746

c-C_7^+ (X^2A_1) (XII-C_7^+)			
	Calc.[b]		Calc.[b]
E	− 265.589736	C1C2C3	106.5
E_r	0.0	C2C3C4	147.6
A_e	5882.485	C3C4C5	114.5
B_e	4877.818	C2C1C7	138.7
C_e	2666.625	$\omega(a_1)$	2042, 1816, 1384, 1059, 939, 441
C1-C2	1.3452	$\omega(b_1)$	559, 342
C2-C3	1.3210	$\omega(b_2)$	3412, 1859, 1210, 660, 474
C3-C4	1.2994	$\omega(a_2)$	572, 331
C1-C7	1.2758		

[a] g = Gas phase; m = Ar, Ne, Kr matrices.
[b] c-C_7^+ harmonic frequencies have been obtained with MP2/aug-cc-pVTZ.

theory (B3LYP), XII-C_7^+ is a transition state lying −0.85 eV below the linear form. By contrast, it represents the most stable isomer at the RCCSD(T) level of theory, where a strong stabilization (of 1.77 eV) in favor of I-C_7^+ is found (see Figure 1). At the (R)CCSD(T)-F12 level, the C_7 ionization energy (IE) was determined to be 10.42 eV when the zero point vibrational energy correction is considered. IE is deduced as the energy difference between the energies of the linear forms I-C_7 and I-C_7^+ ($l \rightarrow l^+$). Our value is little bit higher than the previous one calculated by Deleuze *et al.*[59] (IE = 9.9 eV). For the energy difference between the absolute minimum structures of I-C_7 and XII-C_7^+ ($l \rightarrow c^+$), it is calculated 9.1 eV.

The RCCSD(T)-F12/aug-cc-pVTZ equilibrium rotational constants of I-C_7, I-C_7^-, I-C_7^+, and XII-C_7^+ were computed to be B_e = 911.792 MHz, B_e = 901.579 MHz, and B_e = 914.563 MHz, and A_e = 5882.485 MHz, B_e = 4877.818 MHz, and C_e = 2666.625 MHz, respectively. To evaluate the quality of these results, our previous estimations of rotational

TABLE III. MRCI/aug-cc-pVTZ vertical excitation energies (E, in eV) to the lowest electronic states of C_7, C_7^-, and C_7^+. We also list the prominent electron configuration quoted at equilibrium geometry of the corresponding ground state.

Symmetry	E	Prominent configuration	Expt.	Previous calculation
		***l*-C_7**		
$X\ ^1\Sigma_g^+$	0.00[a]	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4$	0.00	0.0 [Refs. 8 and 12]
$^3\Sigma_u^+$	1.97	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$	1.71 [Ref. 28]	1.89 [Ref. 8], 1.07 [Ref. 12]
$^3\Delta_u$	2.20	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		1.79 [Ref. 8], 1.19 [Ref. 12]
$^3\Pi_u$	2.20	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		2.16 [Ref. 8], 1.13 [Ref. 12]
$^3\Pi_g$	2.21	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		1.92 [Ref. 8], 1.14 [Ref. 12]
$^3\Sigma_u^-$	2.21	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		2.0 [Ref. 8], 1.25 [Ref. 12]
$^1\Delta_u$	2.36	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		1.54 [Ref. 8], 1.23 [Ref. 12]
$^1\Sigma_u^-$	2.43	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		2.00 [Ref. 8], 1.25 [Ref. 12]
$^1\Pi_u$	2.98	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$	2.29 [Ref. 26]	2.64 [Ref. 8], 1.5 [Ref. 12]
$^1\Pi_g$	2.99	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^1$		2.26 [Ref. 8], 1.51 [Ref. 12]
$^1\Sigma_u^+$	3.04	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^1$		5.54 [Ref. 8], 3.61 [Ref. 12]
$^5\Sigma_u^-$	3.40	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		
$^5\Sigma_g^+$	3.87	$(8\sigma_g)^2\ (2\pi_u)^2\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^5\Pi_g$	3.88	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		
$^5\Pi_u$	3.89	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^3\Delta_g$	4.01	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^1$		2.42 [Ref. 8], 2.4 [Ref. 12]
$^3\Sigma_g^+$	4.18	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2(1\pi_g)^3(2\pi_g)^1$		2.59 [Ref. 8], 2.78 [Ref. 12]
$^3\Sigma_g^-$	4.28	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^1$		3.38 [Ref. 8], 2.69 [Ref. 12]
$^1\Delta_g$	4.43	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^1$		2.75 [Ref. 8], 2.69 [Ref. 12]
$^1\Sigma_g^-$	4.50	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^1$		3.31 [Ref. 8], 2.87 [Ref. 12]
$2^1\Sigma_g^+$	4.48	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^1$		2.31 [Ref. 8], 3.37 [Ref. 12]
$2^3\Pi_g$	4.68	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		3.31 [Ref. 12]
$2^3\Pi_u$	4.69	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^1$		3.31 [Ref. 12]
$^3\Phi_u$	4.77	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^3\Phi_g$	4.77	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		
$2^1\Pi_g$	5.28	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		4.09 [Ref. 12]
$2^1\Pi_u$	5.38	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		4.09 [Ref. 12]
$^1\Phi_g$	5.52	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^1\Phi_u$	5.56	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		
$^5\Delta_u$	5.60	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^2$		
$^5\Sigma_u^+$	5.92	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^2$		
$^5\Sigma_g^-$	6.03	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^3$		
$^5\Delta_g$	6.34	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^3$		
$^5\Phi_u$	6.89	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^1$		
$^5\Phi_g$	6.90	$(8\sigma_g)^1\ (2\pi_u)^3(3\pi_u)^1(7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^1$		
		***l*-C_7^-**		
$X\ ^2\Pi_g$	0.00[b]	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^1$	0.00	0.00 [Refs. 10 and 11]
$^4\Pi_u$	1.93	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^2\Pi_u$	2.28	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$	1.98 [Refs. 10 and 29]	2.77 [Ref. 11]
$^4\Sigma_g^-$	2.37	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		
$^4\Sigma_u^-$	2.37	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		
$^2\Phi_u$	2.41	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		2.63 [Ref. 11]
$2^2\Pi_u$	2.62	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$	2.52 [Ref. 29]	2.92 [Ref. 11]
$3^2\Pi_u$	2.82	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		3.03 [Ref. 11]
$^2\Sigma_g^-$	3.14	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		3.01 [Ref. 11]
$^2\Sigma_u^-$	3.14	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		3.07 [Ref. 11]
$^2\Sigma_g^+$	3.20	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		3.45 [Ref. 11]
$^2\Sigma_u^+$	3.20	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		3.50 [Ref. 11]
$^2\Delta_g$	3.20	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4(2\pi_g)^2$		3.14 [Ref. 11]
$^2\Delta_u$	3.20	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4(2\pi_g)^2$		3.16 [Ref. 11]
$^4\Pi_g$	3.98	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3(2\pi_g)^2$		
		***l*-C_7^+**		
$X\ ^2\Sigma_u^+$	0.00[c]	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^1\ (1\pi_g)^4$		
$^2\Sigma_g^+$	−0.01	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^4$		
$^2\Pi_u$	0.09	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^2\ (1\pi_g)^4$		
$^4\Pi_u$	1.08	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		

TABLE III. (*Continued*.)

Symmetry	E	Prominent configuration	Expt.	Previous calculation
$^2\Pi_g$	1.51	$(8\sigma_g)^2\ (2\pi_u)^4\ (6\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		
$^4\Delta_u$	1.60	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$^4\Delta_g$	1.61	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$^4\Sigma_u{}^+$	1.63	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4\ (2\pi_g)^1$		
$^4\Sigma_g{}^+$	1.63	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$^4\Pi_g$	1.98	$(8\sigma_g)^2\ (2\pi_u)^2\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		
$2^2\Pi_u$	2.12	$(8\sigma_g)^1\ (2\pi_u)^4\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$2^2\Pi_g$	2.39	$(8\sigma_g)^2\ (2\pi_u)^4\ (7\sigma_u)^2\ (1\pi_g)^3$		
$^2\Phi_g$	2.48	$(8\sigma_g)^2\ (2\pi_u)^2\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		
$^2\Sigma_g{}^-$	2.60	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$^2\Sigma_u{}^-$	2.61	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		
$^2\Delta_u$	2.63	$(8\sigma_g)^1\ (2\pi_u)^3\ (7\sigma_u)^2(1\pi_g)^4(2\pi_g)^1$		
$^2\Delta_g$	2.64	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
$2^2\Sigma_g{}^+$	2.67	$(8\sigma_g)^2\ (2\pi_u)^3\ (7\sigma_u)^1(1\pi_g)^4(2\pi_g)^1$		
		c-$C_7{}^+$		
X $^2A_1$	0.0	$(10a_1)^2\ (11a_1)^1\ (2b_1)^2(7b_2)^2(1a_2)^2$		
$^2B_1$	1.38	$(10a_1)^2\ (2b_1)^2(7b_2)^2(1a_2)^2(2a_2)^1$		
$^2B_2$	1.60	$(10a_1)^2\ (2b_1)^2(7b_2)^2(1a_2)^2(2a_2)^1$		
$^2A_2$	2.01	$(10a_1)^2\ (2b_1)^2(7b_2)^2(8b_2)^2(1a_2)^1$		
2^2A_1	2.28	$(10a_1)^2\ (12a_1)^1\ (2b_1)^2(7b_2)^2(1a_2)^2$		
2^2B_2	2.97	$(10a_1)^2\ (2b_1)^2(7b_2)^2(8b_2)^2(1a_2)^1$		
$^4A_1$	3.29	$(10a_1)^2\ (11a_1)^1\ (2b_1)^2(7b_2)^2(1a_2)^2$		
$^4A_2$	3.29	$(10a_1)^1\ (11a_1)^1\ (2b_1)^2(3b_1)^1(7b_2)^2(1a_2)^2$		
$^4B_2$	3.32	$(10a_1)^1\ (11a_1)^1\ (2b_1)^2(7b_2)^2(8b_2)^1(1a_2)^2$		
$^4B_1$	3.50	$(10a_1)^1\ (11a_1)^1\ (2b_1)^2(3b_1)^1(7b_2)^2(1a_2)^2$		
		Electron affinity (EA) and ionization energy (IE)[e]		
		EA (eV) = 2.73 eV	3.358 [Ref. 24]	
		IE (eV) = 10.18 ($l \rightarrow l^+$)		
		IE (eV) = 8.59 ($l \rightarrow c^+$)		

[a]E = −265.624595 a.u.
[b]E = −265.724890.
[c]E = −265.250339 a.u.
[d]E = −265.308956 a.u.
[e]Zero point vibrational energy neglected.

constants of other carbon chains, i.e., for C_4Si, we can certify that explicitly correlated coupled cluster theory leads to equilibrium rotational constants identical to the ones determined with RCCSD(T) at the complete basis set.[51] The B_e parameters were further employed to evaluate B_0, which are at less than 2.5 MHz from the experimental value.[51] In the literature, the few existing data correspond to the neutral form I-C_7. With infrared laser absorption spectroscopy, B_0 was determined to be 917.755 MHz.[16] Previous RCCSD(T) calculations of Botschwina[13] lead to B_e (I-C_7) = 916.8 MHz. In Ref. 9, the difference B_e(I-C_7) − B_e(I-$C_7{}^-$) was computed to be 9 MHz in a good agreement with our calculations. For anionic and cationic forms of C_7, our work represents the first determination of these quantities that may be used for assigning their experimental and astrophysical spectra whenever measured.

In Table II, the harmonic wavenumbers for the three absolute minima are provided. For I-C_7, some calculated band positions corresponding to the ν_3, ν_4, ν_5, and ν_7 modes are compared with previous infrared experimental data in gas phase,[14–16,21,23,24] or measured in Ar, Ne, or Kr matrices.[17–19,22,26] Although we provide all the eleven I-$C_7{}^-$ frequencies, only the stretching modes are reliable. I-$C_7{}^-$ is a Renner-Teller molecule ($X^2\Pi_g$) where an important spin-orbit effect can be expected (A_{so} = 26.8 cm^{-1}, Ref. 10). Finally, we compute all positive real frequencies for XII-$C_7{}^+$ using RCCSD(T)-F12, although a TS is predicted at B3LYP level. No doubt, explicitly correlated results should be viewed as more reliable.

Electronic states of C_7

Table III lists the CASSCF/MRCI/aug-cc-pVTZ vertical excitation energies to the lower electronic exited states of I-C_7, I-$C_7{}^-$, I-$C_7{}^+$, and of the cyclic XII-$C_7{}^+$ using the active space described in the Computational Details section. These calculations were performed at the CCSD(T)-F12/aug-cc-pVTZ ground electronic states geometries (Table II). A total amount of 35, 14, and 18 states has been computed for the three linear species I-C_7, I-$C_7{}^-$, I-$C_7{}^+$, and 10 states for the cyclic one. All I-$C_7{}^-$ states located lower than 3.8 eV (i.e., the electron affinity of this species) can be bond states

with minimum energy structures lying below the neutral potential. At MRCI level, the EA is reduced to 2.73 eV without considering the zero point vibrational energy correction. Nevertheless, the present statement remains valid for most of the anionic states.

Lower electronic states can play important roles in the reactivity of small carbon chains. They can be also used for detectability purposes in astrophysical sources.[38] For neutral C_7, 35 electronic states (13 singlets, 12 triplets, and 10 quintets) lying below 5.6 eV were calculated. The first excited state is a triplet $^3\Sigma_u^+$ of 1.97 eV, which is close to the experimental value of 1.71 eV of Khono *et al.*[28] The first singlet $^1\Delta_u$ lies at 2.36 eV. The $^3\Pi_u$ and $^1\Pi_u$ states were found at 2.19 eV and 2.98 eV. The latter compares well with the value given by Forney *et al.*[26] (2.29 eV), which was measured in Neon matrix. In Table III (last column), previous vertical excitations of Kobulszewski[8] and Giuffreda *et al.*,[12] computed with MRDCI(Q) and ADC(2) theories and short basis sets, are shown. Both sets of results really differ and also differ from our calculations performed at a higher level of theory. For example, the first excited electronic state is identified as $^1\Delta_u$ and $^3\Sigma_u^+$ in Refs. 8 and 12. Our first state is a $^3\Sigma_u^+$, which supports Kohno *et al.*[28] interpretation of the band observed a 1.71 eV by anion photoelectron spectroscopy observations to a triplet of $^3\Sigma_u^+$ or $^3\Sigma_u^-$ or $^3\Delta_u$ symmetry. To our knowledge, there are no previous theoretical excitation energies for quintet electronic states.

For linear C_7^-, present excitation energies are compared with the experimental data of Lakin *et al.*,[10] who have also performed *ab initio* calculations and with the theoretical energies of Cao *et al.*[11] C_7^- is a Renner-Teller molecule whose ground electronic state is $X^2\Pi_g$. Two close laying states, namely, the $^4\Pi_u$ and $^2\Pi_u$ states, follow in energy at 1.93 eV and 2.28 eV, respectively. The $^2\Pi_u$ state was observed at 1.98 eV.[10,29] The second state $^2\Pi_u$ is localized here at 2.62 eV, i.e., 0.1 eV off from the experimental value (=2.52 eV[29]). The spin-orbit constants for these two states were estimated to be A_{SO} $(X^2\Pi_g) = 26.8$ cm^{-1} and $A_{SO}(^2\Pi_u) = -6.2$ cm^{-1}.[10]

To our knowledge, there are no available experimental data concerning the electronic states of C_7^+. In Table III, we provide 18 states of I-C_7^+ below 2 eV and 10 states for XII-C_7^+ lying below 4 eV, for which, the two first excited electronic states, $^2B_1$ and $^2B_2$, are at 1.38 eV and 1.60 eV, respectively. The lowest quartets $^4A_1$ and $^4A_2$ lie at 3.29 eV. I-C_7^+ presents two electronic states $X^2\Sigma_u^+$ and $^2\Sigma_g^+$ very close in energy. The vertical excitation energy is evaluated to be 63 cm^{-1} (RCCSD(T)/aug-cc-pVTZ), 71 cm^{-1} (RCCSD(T)/aug-cc-pVTZ), and -115 cm^{-1} (MRCI/aug-cc-pVTZ). Both states are coupled vibronically that may complicate the pattern of their rovibronic spectra. Standard nuclear motion treatment methodologies are not valid for the prediction of such spectra. Only full variational treatments on full dimensional potential energy surfaces lead to reliable data. This is out of the scoop of the present investigations.

CONCLUSIONS

The number of possible isomers C_n carbon chains increases fast with the number of carbon atoms. A search of stationary points achieved using B3LYP/aug-cc-VTZ leads to a total of twelve C_7 structures and fifteen and fourteen minima for the charged species, C_7^- and C_7^+, respectively. The most stable geometries of the neutral and anion species are two linear forms, I-C_7 ($X^1\Sigma_g^+$) and I-C_7^-($X^2\Pi_g$) (or *l*-C_7 and *l*-C_7^-), and for the cation, the lowest energy corresponds to a 7-atom cyclic structure XII-C_7^+ (X^2A_1) (or c-C_7^+). This last structure is strong dependent on electronic correlations. Thirty five electronic states of C_7, suitable to be involved in reactive processes, lie below 7 eV. Fourteen metastable electronic states of C_7^- have been found below 3.5 eV. For *linear*-C_7, we compute the electron affinity and the ionization energy to be 3.38 eV and 10.42 eV, respectively.

Some conclusions of this paper can be important for astrophysical searches. First, the excitation energy to the excited electronic states is large enough to assure the stability of C_7. The ground state rovibrational spectrum is more "clean" than in other carbon chains. In addition, whereas the most stable linear forms of C_7 and C_7^- present a zero-dipole moment, some isomers of very low energy show permanent dipole moments that make them suitable for radioastromomical observations.

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